Syntroleum

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Ms. Linda Bluestein
U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy/
Office of FreedomCAR and Vehicle Technologies
Docket No. EE-RM-02-200, EE-2G
1000 Independence Avenue, SW
Washington, DC 20585-0121

Re: A Discussion of Issues Pertinent to the Rulemaking to Designate FTD fuels as Alternative Fuels Under Section 301(2) of the Energy Policy Act of 1992

Dear Ms. Bluestein:

Please find enclosed a copy of Syntroleum's written response to the technical questions you raised in your referenced workshop discussion paper.

If you have any questions with regard to the enclosed information, please feel free to contact me.

Sincerely,

R. Steven Woodward
Manager Fuel Sales
Syntroleum Corporation

Enclosure

RSW/kp

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Syntroleum Response to DOE Questions Pertinent to the Rulemaking to Designate FTD Fuels As Alternative Fuels Under Section 301(2) of the Energy Policy Act of 1992

DOE EPAct Question 1:
How should DOE define natural gas-based diesel fuels, and particularly FTD fuels, if designation is ultimately limited to that process?

Syntroleum agrees with the DOE that for purposes of designating FTD as an alternative fuel under EPAct, there needs to be a definition of the feedstock such as "naturally occurring natural gas." Further, we support the assertion that FTD made from coal and/or biomass would already be considered an alternative fuel under the original guidelines of EPAct. Additionally, we support the assertion that any FTD that is derived from petroleum waste or refinery by-product streams should not be considered.

Syntroleum would suggest that the definition include natural gas from fossil sources with a minimum methane content specified and to include methane from landfill gas. The definition should be broad enough to encompass natural gas that can be produced and recovered by current technology and by future technologies. For example, natural gas from methane hydrates should be included.

DOE EPAct Question 2:
DOE requests comments on analysis provided by the Argonne National Laboratory (ANL) and the National Renewable Energy Laboratory (NREL), which will be used for making a determination regarding designation of FTD fuels.

Syntroleum has reviewed the referenced documents and generally supports the analytical work done and the results indicated. Where appropriate, we have made specific comments on certain areas of both documents in response to the questions posed by the DOE.

DOE EPAct Question 2a:
DOE also requests that interested parties submit any additional emissions data not cited in the NREL report.

In preparing their assessment of the emissions benefits of FTD, NREL referenced an extensive list of reports, papers and publications. While several Society of Automotive Engineers (SAE) papers were included in the reference list, Syntroleum would direct NREL to additional SAE papers and technical reports that discuss the results of various emission tests comparing FTD to conventional and ultra-low sulfur fuels. These reports are listed in Attachment 1.

DOE EPAct Question 3:
Should DOE set process energy use limits in its EPAct designation process to ensure that qualifying FTD fuels provide substantial energy security benefits?

Syntroleum does not believe that process energy use limits should be considered in the context of providing for U.S. energy security. The issue of U.S. energy security is a much broader issue than plant operating efficiencies. The cumulative effect of improving the conversion efficiencies of a few FTD plants would do little to offset the large (and growing) amount of foreign crude oil we import each year. We know of no established energy use limits imposed on other EPAct alternative fuels, some of which are imported into the U.S. Also, we know of no energy use limits imposed upon the amount of energy it would take for the U.S. refining industry to comply the with the EPA's mandated reduction of the sulfur content in conventional diesel to 15 ppm. Perhaps more importantly, there are no energy use limits imposed on domestically produced FTD. Taking this posture on FTD has no established precedent. Moreover, under those authorities granted to the DOE under Section 504(c) of EPAct, the DOE is specifically enjoined not to mandate marketing or pricing practices for alternative fuels. By setting process energy use limits on FTD plants, the DOE would be establishing in a "defacto" fashion FTD production costs. Such additional costs would then have to be borne in the market place by the FTD producer, thus affecting his pricing practices.

Being produced from natural gas, any FTD supplied to the U.S. alterative fuel market would decrease our dependence on imported oil thus increasing our energy security. Oak Ridge National Laboratory (ORNL) supports this position. In a white paper prepared for the DOE, "An Assessment of Energy and Environmental Issues Related to the Use of Gas-to-Liquid Fuels in Transportation, November 1999," ORNL was very clear on their findings on the issue of energy security as it pertains to the production of FTD outside the U.S. Quoting from this document,

> "It is very likely that emergence of a G-T-L industry would enhance U.S. energy security, despite the fact that much, if not most, of the fuel would be imported."
>
> "From the economic perspective, improving energy security becomes a matter of reducing the quantity of oil imported, increasing the economy's ability to substitute other energy sources for oil and reducing the potential market power of oil producers."

The document further supported this last statement by modeling the world petroleum supply, demand and pricing forces, considering the production of G-T-L supply by both OPEC and non-OPEC countries. This analysis concluded that,

> "The existence of a significant substitute for petroleum would change market competition in at least three significant ways. First, the cartel's pricing problem would now include the joint maximization of profits over two feedstocks instead of just one. This makes the pricing formula considerably more complex. Second, the creation of a new substitute increases the world price elasticity of crude oil demand, which would lower the optimal monopoly price of oil, whether or not the cartel chooses to produce any G-T-L's. Third, because the distribution of gas reserves, there is a change in the balance of power within the cartel that could affect its internal decision making, most importantly its ability to agree on and enforce optimal monopoly pricing decisions."

DOE EPAct Question 3a:
If so, which levels are appropriate?

Syntroleum does not believe that process energy use limits should be considered as part of the DOE rulemaking. Please see our comments above.

DOE EPAct Question 4:
How should DOE balance its determinations about designating fuels if the fuels provide substantial benefits in some areas with regard to section 301(2) criteria, while being a slight detriment to others (e.g., positive attributes regarding criteria pollutants versus a slight increase in greenhouse gas emissions)?

In your discussion paper, you presented a list of the environmental impacts that the DOE was to consider with regard to one of the three criteria for rulemaking contained in Section 303(2), "substantial environmental benefits". Those were:

- Criteria pollutant emissions (principally from vehicles)
- Greenhouse gas emissions (from vehicles and fuel production/distribution)
- Toxic pollutant emissions (principally from vehicles)
- Other environmental impacts, such as groundwater pollution, marine pollution, etc. as related to biodegradation, ecotoxicity, etc.

Syntroleum believes that there are basic differences in judging between the benefits of FTD as it pertains to criteria pollutants, toxic pollutants, biodegradability and ecotoxicity and the quantification of potential FTD greenhouse gas emissions.

Analytical testing and examination of the measured results determine the reduction in criteria pollutants. NREL concluded that there is a 99% confidence level in the analysis that absence of sulfur, aromatic hydrocarbons and the higher cetane numbers in FTD reduces all regulated (or criteria) pollutants. Notwithstanding their comments on the statistical significance of the individual tests comparing FTD emissions to conventional and low sulfur diesel fuels, it is conclusive that the performed tests report significant emission reductions using FTD. FTD has also been shown to reduce air toxics and has been shown to be biodegradable and to have low ecotoxicity (see Syntroleum's response to Question 9.)

On the other hand, the comparison of potential greenhouse gas emissions between FTD production and diesel production is not a measurement at all, but a subjective analysis. It is based on a detailed analysis of a series of assumptions. The fact that the analysis includes probability distribution functions speaks to the subjective nature of the data used. In developing the assumptions for the FTD process efficiencies, ANL used detailed information submitted by the petitioners as well as other data from a variety of sources. This data and other assumptions were used to develop a range of possible operating conditions meant to represent high and low probabilities of energy use and GHG emissions. Also, ANL included separate cases for stand-alone FTD plants, FTD plants capable of exporting steam and/or electricity and a FTD plant with flared gas as a feedstock. However, no attempt was made to model a base case scenario whereby certain volumes of FTD would be produced wherein certain percentages of these production cases would be included.

On the comparative side, for the conventional diesel and low-sulfur diesel, ANL used default fuel characteristics from their GREET 1.6 model and established parametric assumptions for production and refining efficiencies. This comparative information is entirely subjective. The various process pathways by which hundreds of U.S. refiners will reduce the sulfur content of on-road diesel fuel from 500 ppm to 15 ppm (in order to comply with the EPA ruling to produce this fuel by the year 2006) is not clearly defined.

That being the case, are the assumed energy requirements and the resulting greenhouse gases in the two diesel comparative cases accurate enough to suggest that the FTD will have more or less emissions? Additionally, there is no consideration given that the use of FTD as an alternative fuel will replace other alternative fuels being used in EPAct fleets. In fact, a good argument could be made that FTD will replace conventional gasoline, since it is being used in over 80 percent of the dual fueled alcohol vehicles.

Based on these considerations, Syntroleum believes that there is not enough objective information to suggest that greenhouse gases from FTD will or will not be greater than the fuel or fuels they ultimately replace. However, if a greenhouse gas comparison must be made, then Syntroleum contends that the data prepared by ANL be assessed on a more rigorous statistical basis considering the various FTD plant configurations and feedstock sources.

There are numerous areas of the world where a large amount of the natural gas is being vented, flared and/or leaked. To say that future FTD plants would not use feedstocks or that there would be some finite life to the use of these gas sources is an entirely subjective opinion on the part of the DOE. Even if a small percentage of vented and flared gas were used for a short period of time, the positive GHG emissions benefits would certainly offset other stand-alone plants using conventional natural gas. In a similar argument, to give no statistical weight to FTD plants that would produce exportable steam or power is again a subjective opinion. No mention has been made concerning the possibility of CO_2 sequestration that would be economically viable in many of the potential FTD plant locations. In many cases, the feedstock for the FTD plant would come from an oil or gas production area that would benefit from and often requires reservoir pressure maintenance. Again, as in the case of flared or vented gas, even a small percentage of FTD plants operated in such a fashion as to sequester CO_2, would have a very positive benefit on the aggregate FTD plant greenhouse gas inventory.

Finally, one should bear in mind that FT technology has just begun to embrace the various possibilities to improve efficiencies that would go directly to the plants economic robustness. Economic drivers will become environmental drivers.

DOE EPAct Question 4a:
Is such an approach desirable?

Based on the considerations detailed above, Syntroleum believes the greenhouse gas comparison is at best neutral at this point in time. Moreover, we would suggest that a longer-term view would demonstrate a much different position with regard to greenhouse gas emissions of FTD production compared to the fuel or fuels it ultimately replaces. Therefore, Syntroleum believes that the DOE should base the determination of substantial environmental benefits primarily on measurable reductions of criteria pollutants, reductions in air toxics, biodegradability and ecotoxicity.

DOE EPAct Question 5:
DOE requests comments on findings in NREL's report about NOx emissions benefits of 6-20 percent (compared to post-2006 diesel fuels) related to control of fuel aromatic content and cetane number.

Syntroleum agrees with the DOE findings concerning NOx. Several of the SAE papers referred to in Attachment 1 support this assertion.

DOE EPAct Question 5a:
Should these benefits be considered ``substantial'' with regard to section 301(2) criteria?

Yes, Syntroleum believes that NOx benefits should be considered substantial.

DOE EPAct Question 6:
DOE is seeking additional data on actual test and control fuels for FTD when used in later-model diesel engines to gauge how fuel composition affects emissions from these engines.

Several of the SAE papers referred to in Attachment 1 provide this data.

DOE EPAct Question 7:
What parameters should be set for aromatics, cetane, sulfur, and other standards to assure emissions reductions based on NREL's findings or other sources of information?

Syntroleum supports the DOE recommendation that the designation of FTD fuels should be based on a uniform set of specifications for a neat fuel. Syntroleum would propose that FTD meet all current and future ASTM D975 specifications with the following exceptions and inclusions:

- A maximum sulfur content of 1 ppm by mass
- A minimum cetane number of 70
- A maximum aromatics content of 500 ppm by volume
- A maximum oxygen content of 100 ppm by volume

To the extent that the above fuel properties are already included as a specification in ASTM D975, the ASTM test method by which that property is measured will need to be changed in the FTD specification to reflect the degree of accuracy required to measure the appropriate specification limits.

The above specifications would be for un-additized FTD. Each individual producer would be responsible for developing appropriate additive packages for their product.

DOE EPAct Question 7a:
Also, will FTD fuels in the lower end of the aromatics range result in materials compatibility problems?

No. While there have been seal problems reported with past uses of ultra-low sulfur diesel fuels in older engines, based on discussions with diesel engine manufacturers, Syntroleum has the understanding that the seal material used in modern diesel engines can tolerate the absence of aromatic compounds in FTD.

DOE EPAct Question 7b:
Should polyaromatic content be included in addition to, or in lieu of, a limit on total aromatics?

No. The proposed 500 ppm limit we propose for total aromatic content of FTD will be sufficient.

DOE EPAct Question 7c:
Should paraffin content be used to assure emissions reductions, and if so, do both normal- and iso-paraffin content need to be specified?

Yes. Syntroleum believes that FTD should contain at least 90 percent paraffin by volume. We do not see the need to specify the normal- and iso-paraffin content.

DOE EPAct Question 8:
There are various ways DOE might designate fuels with relation to greenhouse gas (GHG) emissions. The discussion paper located at the website address listed above suggests three such ways to view this question. DOE requests comments on which option would be most appropriate, and what levels of GHG emissions should be set if a particular option is chosen.

Syntroleum believes that the DOE should designate all FTD meeting the defined fuel parameters as alternative fuels based on the rational that GHG emissions are not so significant as to offset the expected criteria pollutant emission benefits.

DOE EPAct Question 9:
DOE seeks any information and data collected about toxicity issues and ecotoxicity/biodegradability issues related to FTD.

Being comprised of greater than 99% paraffinic hydrocarbons, Syntroleum FTD has very little environmental impact. In addition to being highly biodegradable, testing for aquatic toxicity has demonstrated little impact to trout, mysid shrimp, and aquatic bacteria. Animal toxicological studies also showed FTD to have minimal problems. Rabbit skin and eye irritation was minimal, and rat oral toxicity was extremely low. Attachment 2 has detailed test information on toxicity and biodegradability of Syntroleum FTD.

Additionally, Syntroleum would refer the DOE to the results of a project sponsored by the DOE Office of Transportation Technologies, "Chemical Characterization of Toxicologically Relevant Compounds From Diesel Emissions". In this research project various gaseous exhaust toxins were collected from a modern DaimlerChrysler OM611 CIDI diesel engine fueled by FTD and compared to emissions of a EPA 2D certification fuel (a typical CARB diesel), a low-sulfur diesel fuel having only 1 ppm of sulfur and a blend of DDM and low sulfur diesel. Compared to these fuels, FTD was either ranked the lowest fuel for measured engine out emissions of all EPA criteria pollutants and the four toxic air pollutants (formaldehyde, acetaldehyde, benzene and 1,3-butadiene) or was in the lowest statistical significant group. A full copy of that report attached.

DOE EPAct Question 10:
DOE requests comments on limiting oxygenated compounds in FTD fuels or suggestions on alternative approaches. Possibilities are outlined in the discussion paper.

Syntroleum believes that the inclusion of oxygenated compounds in FTD fuels should be limited to 0.10 volume percent.

DOE EPAct Question 11:
Are any of FTD fuels' characteristics sufficiently unique to justify inclusion of specific additives to assure that inherent environmental benefits are not degraded or negated due to negative impacts on engine components or emission control systems?

Please see our comments in response to Question 7. Syntroleum believes that FTD specifications should be on neat un-additized fuel. The addition of additives to FTD should be addressed on a commercial basis on an as-required basis. Specifically addressing the issue of lubricity, it is our belief that when conventional diesel is hydrotreated to lower the sulfur content to 15 ppm (or lower at the refinery gate) it will be viewed as having the same problem with lubricity as FTD. Appropriate ASTM committees are addressing this issue of lubricity in low sulfur fuel and a specification for lubricity will probably be added to the ASTM D975 specifications.

DOE EPAct Question 12:
Are there other issues that DOE should consider related to Fischer-Tropsch diesel fuel production and use relative to its possible designation as an alternative fuel?

Perhaps the biggest challenge for alternative fuels under EPAct is affordability. Most alternative fuels require additional expense to either modify vehicles for their use or to install a special purpose fuel system in the vehicle. In many cases, it is the cost of the fuel and the fuel delivery system that limits the use of the fuel in the vehicles intended to use it, thus creating the much discussed "chicken and egg" problem associated with alternative fuels.

FTD meets all of the criteria to be a successful alternative fuel, i.e. it is safe, reliable and affordable. Not only does FTD offer substantial reductions in criteria pollutants, it has a very low-toxicity and is highly biodegradable. There is nothing more reliable in the road transportation industry than a diesel engine. Diesel engines are simple to operate and easy to maintain even with advanced technology. FTD diesel can be transported, stored and dispensed using the same type of equipment as conventional diesel. FTD does not increase the cost of a new vehicle in order for it to be used, it does not increase (and probably will decrease) vehicle maintenance needs, and it does not require modification of and/or the addition of fuel infrastructure. Once cleaned to remove traces of higher sulfur, most of the existing equipment in a central fleet fueling location is ready to store and dispense FTD diesel.

Alternative vehicles with clean diesel engines using FTD would be approximately 40 percent more efficient than spark ignition engines used in many dual fueled alternative vehicles. Such FTD fueled vehicles would do more work and travel more miles while using less fuel. An additional benefit of FTD fuels is that they are technology neutral. FTD fuels can be used in current and advanced compression ignition engines, and as a transition to the future, they are fully compatible with diesel electric hybrid vehicle power systems and fuel cells.

Attachment 1. SAE Technical Papers

982489	Consideration for Fischer-Tropsch Derived Liquid Fuels as a Fuel Injection Emission Control Parameter
1999-01-1117	Transient Emissions Comparisons of Alternative Compression- Ignition Fuels
1999-01-2251	On-Road Use of Fischer-Tropsch Diesel Blends
2000-01-1852	Present Day Diesel Engine Pollutant Emissions: Proposed Model for Refinery Bases Impact
2002-01-2725	Impact of Ultra-Clean Fischer-Tropsch Diesel Fuel on Emissions in a Light Duty Passenger Car Diesel Engine
2002-01-2726	Evaluating a Fischer-Tropsch Fuel, Eco-Par TM, in a Valmet Diesel Engine
2002-01-2727	Exhaust Particle Numbers and Size Distributions with Conventional and Fischer-Tropsch Diesel Fuels

Attachment 2. Environmental and Toxicological Testing of Syntroleum Fischer-Tropsch Diesel Fuel

General Conclusions

Being a 100% paraffinic hydrocarbon, Syntroleum Fischer-Tropsch Diesel fuel shows very little environmental impact. Testing for aquatic toxicity has demonstrated little impact to trout, mysid shrimp, and aquatic bacteria, as well as being very high biodegradable. Animal toxicological studies also show minimal problems. Rabbit skin and eye irritation was minimal, and rat oral toxicity was extremely low.

Some of the following terms are commonly used in Ecotoxicity
LC50—Concentration of chemical that is toxic to 50% of the test species.
EC50—Concentration of chemical that causes 50% of the test species to become immobile.
NOEC—Concentration of chemical that has no effect in a test.
LOEC—Lowest concentration of chemical that shows an effect in a test.

Aquatic Toxicology

Numerous tests are available to assess the risk to the environment from unintended exposure to a chemical substance. The risk is based on the ability of a substance to dissolve into an aquatic environment or penetrate soil before it either evaporates or is biodegraded to non-organic species combined with the interaction of the substance with biological organism if and/or when it enters the life zone of that organism.

Through research and consultation with laboratories performing aquatic toxicological tests, the following three tests were deemed important guides to assessing the toxicology of paraffinic Fischer-Tropsch diesel fuel.

96 Hour Trout Static Acute Toxicology Test

This test assesses the danger to species higher in the aquatic food chain from exposure to chemicals. The test involves exposing the trout to different levels of the chemical until a mortality of 50% is reached (LC 50). A higher value in this test indicates lower risk to trout and other aquatic feeders.

Syntroleum F-T diesel fuel showed a LC50 of >1000 mg/liter. No effect was observed at the 1,000 mg/liter test level (NOEC = 1000 mg/L). Conventional diesel fuel typically shows values of 2.43 mg/liter at 48 hours (data from Environment Canada web site). This is mainly due to the aromatic content of the conventional diesel fuel.

Daphnia 48h Static Acute Toxicology Test

Mysid shrimp (*Daphnia magna*) are next down on the food chain and represent a sizable amount of food for fish such as trout. Chemicals that damage this aspect of aquatic biology can cause collapse of the entire chain. Paraffins are typically not highly toxic to mysid shrimp, and the results for Syntroleum Fischer-Tropsch diesel are typical for this class of compounds.

The concentration at which 50% of the mysid shrimp were killed by the Syntroleum S-2 test sample (LC50) was estimated at 11 mg/L. This result is based on the lowest concentration tested that had a measurable effect (LOEC) of 16 mg/L and the highest concentration that had no measurable effect (NOEC) of 8 mg/L. Conventional diesel fuel gave a *Daphnia magna* LC50 of 0.51 mg/L in a similar test (Environment Canada Data).

Microtox®

The Microtox® test estimates the impact of a chemical on bacteria by looking at the decrease in respiration of *Vibrio fischeri*, a bioluminescent aquatic bacteria. Decreased respiration leads to decreased light output by the bacteria, which can be detected quickly by commercially available equipment.

Syntroleum S-2 exhibited a Microtox® Threshold EC50 of 0.94% and EC20 of 0.28%. EC50 and EC20 represent the concentration of a test compound that causes 50% or 20% reduction in respiration as measured by decrease in light produced by the bacteria. Specifications for discharge of drilling fluids (Guide G50) in Alberta, Canada require >75% of the base luminosity for 0.85% concentration. Syntroleum S-2 passed this criteria with >91% luminosity at 0.85% concentration.

Biodegradability

Several tests are available for determining the ultimate biodegradability of organic compounds. Tests for non-volatile compounds use an open system and collect the CO_2 evolved from an aqueous suspension of sewage sludge and the tests compound. This type of test does not work for diesel fuel due to loss of volatile fractions to the air stream. We tested Syntroleum S-2 in the OECD 301D Closed Bottle Test. Results showed a high level of biodegradation, but the results were not high enough in this test to label the sample as readily biodegradable.

This is an expected result based on substantial research into biodegradation. The following is excerpted from a report: "Biodegradation of Petroleum-Based Oily Wastes Through Composting" by W. Ewentu of SLU in Uppsala, Sweden (1996)

> "The most common biological alkanes are C7-C36 and methane. Both saturated and unsaturated hydrocarbons are attacked. Long-chain hydrocarbons (C6-C28) are more vulnerable to attack than short chain (C2-C5). Thus, increasing molecular weight from the C6 to C28 favours decomposition. The unsaturated forms are less easily degraded than the saturated molecules and the branched compounds exhibit a lower susceptibility to the action of microbial enzymes than straight-chain hydrocarbons (Zobell, 1973). However, decreased water solubility reduces somewhat this trend of greater susceptibility at higher carbon numbers. Straight chain paraffins are more easily degraded than aromatics."

Duplicate Closed Bottle Test OECD 301D results were 48% and 57% biodegradable with a minimum of 60% biodegradable needed to claim Ready Biodegradability. Results from one of the two runs were erratic, indicating a need to repeat the test. Other biodegradability tests may actually be more appropriate for diesel fuel samples as well.

Shell has reported on the biodegradability of a similar FT Diesel fuel using a different test, Manometric Respirometry Test OECD 301F. These tests showed roughly 75% ultimate biodegradability and 60% within a 10-day window to qualify for EU biodegradability status. (See "An Evaluation of Shell GTL Diesel—The Environmental Benefits" by Richard H. Clark, et al., presented at the 8th Diesel Engine Emission Reduction Workshop, 25-29 Aug 2002 in San Diego, CA.)

Biodegradability can also be predicted using the EPA EPISUITE Biodegradation Prediction Program (BIOWIN). This program is based on Structure-Activity Relationships of chemical compounds. S-2 biodegradation potential was calculated for each hydrocarbon species correcting for its weighted average content in the fuel mixture. These calculations show primary biodegradation will occur in days, and ultimate biodegradation will occur in weeks, similar to the Shell OECD 301F results.

Summary of Aquatic Toxicology Testing

Screening tests for aquatic toxicity of Syntroleum S-2 FT diesel fuel showed minimal impact on the environment, especially compared to conventional diesel fuel. Although further testing is desirable, there is evidence that FT diesel fuel composed of essentially linear and branched paraffinic molecules should biodegrade quickly in an aquatic environment and not substantially harm aquatic organisms.

Mammalian Toxicology

Potential toxicological impacts on humans and other mammals can be assessed by standard tests on laboratory rabbits and rats. Tests such as skin and eye irritation and oral toxicity are used to establish exposure limits and identify potentially hazardous materials. Syntroleum S-2 was found to be a minimal eye irritant, not a skin irritant, and essentially non-toxic to laboratory rats at high exposure levels.

Primary Eye Irritation Study in Rabbits

Laboratory rabbits were instilled with samples of FT diesel fuel and examined for ocular irritation at 1, 24, 48, and 72 hours. The Maximum Mean Total Score for FT Diesel using the system of Kay and Calandra[1] was 3.7, which is in the low range of minimally irritating (2.6-15.0)

Scale For Scoring Ocular Leasions

MMTS	Irritant Classification
0.0 – 0.5	Non
0.6 – 2.5	Practically non
2.6 – 15	Minimally
15.1 – 25.0	Mildly

[1] Kay, JH, and Calandra, JC, "Interpretation of Eye Irritation Tests", *J. Soc. Cos. Chem*, 1962;**13**:281-289.

Primary Skin Irritation Study in Rabbits

Rabbits are prepared for exposure by removing dorsal hair and the sample was placed on the skin and covered by a gauze pad. After 4 hours, the gauze is removed and the skin wiped free of sample. The skin is rated for irritation at 1, 24, 48, and 72 hours using the Draize Primary Skin Irritation Scoring System. Syntroleum S-2 FT Diesel fuel was found to be non-irritating with a score of 0.3 (<0.5 classified as Non-Irritating).

Primary Skin Irritation Scoring System

PSISS Value	Erythema and eschar Formation	Edema Formation
0	No erythema	No Edema
1	Very slight erythema (barely perceptible)	Very slight edema (barely perceptible)
2	Well-defined erythema	Slight edema (edges of area well defined by definite raising)
3	Moderate to severe erythema	Moderate edema (raised approximately 1 mm
4	Severe erythema (beet redness) to slight eschar formation (injuries in depth)	Severe edema (raised >1 mm and extending beyond area of exposure)

Definitions (Webster Collegiate):
Erythema--abnormal redness of the skin due to capillary congestion
Eschar--a scab formed especially after a burn
Edema--an abnormal infiltration and excess accumulation of serous fluid in connective tissue or in a serous cavity

Acute Oral Toxicity Study in Rats—Limit Test

Laboratory rats, 10 male and 10 female, are fed 5,000 mg/kg by body weight of Syntroleum S-2 FT diesel fuel. The animals were observed for mortality and signs of toxicity and behavioral changes at least once per day for 14 days. Body weights are recorded and the surviving animals were examined internally. All animals survived, gained weight and appeared active and healthy. There were no signs of gross toxicity, adverse pharmacologic effects or abnormal behavior. The single dose acute oral LD_{50} for Syntroleum S-2 is greater than 5000 mg/kg body weight.

Conclusions from Mammalian Toxicology Testing

Syntroleum S-2 FT diesel fuel is minimally irritating to the skin, and non-irritating to the eyes. It is essentially non-toxic at the 5 grams/kg treat rate tested.

B. Chemical Characterization of Toxicologically Relevant Compounds From Diesel Emissions

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

E. Toxic Emissions

F. Ultra-fine Particles

Tasks

8. Safety, Health, and Consumer Acceptance Aspects of Liquid Fuels

Objectives

- Investigate the role of fuels on the engine-out exhaust emissions of potentially toxicologically relevant compounds.
- Determine polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of exhaust particulate matter; gaseous exhaust PAH; other gaseous exhaust "toxics" collected from a diesel engine using various fuel compositions.

Approach

- A DaimlerChrysler OM611 CIDI engine was used to determine the effect of diesel fuel type on toxicologically relevant compounds from engine-out exhaust emissions.
- The engine was controlled by a SwRI Rapid Prototyping Electronic Control System (RPECS).
- The test matrix included 5 fuels (including one oxygenate blend) operated over 5 speed/load points.
- Each speed/load point was devised to hold location of Peak Pressure (LPP) of combustion at 7°ATDC, while maintaining cylinder balance within 5% of the Indicated Mean Effective Pressure (IMEP), with pilot fuel injection disabled.
- Two of the speed/load points were operated at two different pilot fuel injection strategies. One pilot strategy used the stock controller, while the other was to include pilot fuel injection while maintaining the Location of Peak Pressure at a constant.
- Four gaseous "toxic" exhaust emissions were measured.
- Eleven gaseous PAH compounds were measured.
- Seventeen PAH compounds were determined from the soluble organic fraction of the exhaust particulate matter.

Accomplishments

- All fuel tests completed in triplicate for five modes, pilot injection off, LPP operation. Pilot fuel injection effect evaluation for all fuels completed in triplicate for two modes and two pilot fuel injection strategies.
- Statistically significant fuel effects on exhaust emissions identified.
- Oxygenate-containing fuel and Fischer-Tropsch fuel produced the lowest overall toxic gas and PAH exhaust emissions.

Future Directions

- In a follow-on phase, similar investigations will be conducted using an engine with exhaust emission control devices.

Introduction

This program is part of an overall study that examines the effects of alternative diesel fuels including one oxygenated compound (dimethoxymethane) in diesel fuel on the emissions of particulate matter, oxides of nitrogen, and fuel economy. This program addressed the chemical characterization of engine-out emissions of compounds with known or suspected toxicological properties (e.g. carcinogens).

Objective

The goal of this project was to better understand the role of fuels on the emissions of a subset of potentially toxicologically relevant compounds. Objectives of this program were: 1) to measure the polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of particles collected from CIDI engines under a matrix of engine and fuel conditions, 2) to measure the gas-phase polycyclic aromatic hydrocarbons from this engine and, 3) to measure formaldehyde, acetaldehyde, benzene, and 1,3-butadiene using the same conditions that are used to collect particles. These measurements were made on engine-out emissions.

Approach

A standard set of polycyclic aromatic hydrocarbons (PAH) in organic solvent extracts of diesel particles and from the gas phase of diesel emissions were measured in this program. In addition, four toxic air pollutants (as noted above) were quantified. The OM611 CIDI engine was run at five different engine speeds and loads and controlled to hold location of peak pressure of combustion at 7°ATDC. Individual cylinder balance was maintained within 5% of the Indicated Mean Effective Pressure (IMEP), with pilot fuel injection disabled. The engine was also controlled at two speed and load combinations using two different pilot injection control strategies. Particulate filter samples were collected at each load and control condition. The engine operating conditions are shown in Table 1.

Mode	RPM	BMEP, bar	% EGR
M 12	900	0.10	40
M 11	1500	2.62	30
M 10	2000	2.00	30
M 6	2300	4.20	15
M 5	2600	8.80	5

Table 1. OM 611 Engine Operating Conditions

The four toxic air pollutants from mobile sources cited in the Clean Air Act (formaldehyde, acetaldehyde, benzene, and 1,3-butadiene) were measured in triplicate at each of the points discussed above. The five test fuels, along with selected fuel properties are shown in Table 2.

The particulate matter was sampled from a 203mm-dilution tunnel using carbon dioxide tracer for determining dilution ratio. A polyurethane foam and XAD-2 resin trap were utilized for sampling gas phase PAH compounds. Soluble phase PAH compounds were extracted from 90 mm filters.

Fuel (Code)	H, wt %	C, wt %	O, wt %	Cetane Number	Sulfur, ppm	Aromatics, wt %
California Reference Diesel Fuel (CA)	13.4	86.4	0.2	45	176	18.9
Low-Sulfur Diesel Fuel (ALS)	14.4	85.6	0.0	63	1	9.0
Fischer-Tropsch Diesel (FT-100)	15.1	84.8	0.1	84	0	0.2
Oxygenate Blend: 15% Dimethy-oxymethane in ALS (ADMM15)	13.7	81.6	4.7	59	< 2	8.2
EPA 2D Certification Fuel (DF-2)	13.0	86.7	0.3	44	337	30.3

Table 2. Toxicity Test Fuels

Mode	Mode Weights, seconds
Mode 11	600
Mode 10	375
Mode 6	200
Mode 5	25
Total	1,200

Table 3. Weighting Factors for Engine-Out Emissions

Rank	HC	CO	PM	SOF	NO_x	CO_2
Highest	DF-2	DF-2	DF-2	DF-2	DF-2	ADMM15
	CA	CA	CA	CA	ADMM15	DF-2
	ALS	ALS	ALS	ALS	FT-100	CA
	ADMM15	ADMM15	ADMM15	ADMM15	CA	ALS
Lowest	FT-100	FT-100	FT-100	FT-100	ALS	FT-100

Table 4. Fuel Rank Order from ANOVA for Weighted Average Regulated Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

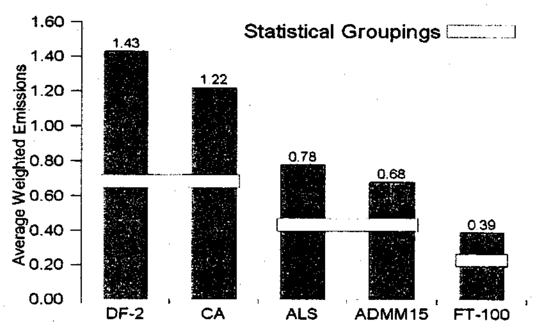

Figure 1. Test Fuel Hydrocarbon Weighted Average Mass Emissions (g/kWh)

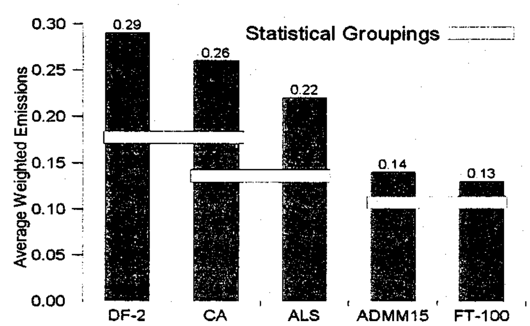

Figure 2. Test Fuel Weighed Average Particulate Matter Mass Emissions (g/kWh)

Benzene and 1,3-Butadiene were collected in a sample bag from the dilution tunnel sample zone. Formaldehyde and Acetaldehyde were trapped on a DNPH adsorbent cartridge from the dilution tunnel sample zone.

Discussion

Fuel comparisons utilizing the Ad-Hoc Fuels Group Mode Weighting Factors shown in Table 3 were made for brake specific exhaust emissions with the engine operated under LPP control with pilot fuel injection turned off.

Rank	Benzene	1,3 Butadiene	Formaldehyde	Acetaldehyde
Highest	CA	CA	DF-2	DF-2
	DF-2	DF-2	ALS	ALS
	ALS	ALS	CA	CA
	FT-100	ADMM15	ADMM15	ADMM15
Lowest	ADMM15	FT-100	FT-100	FT-100

Table 5. Fuel Rank Order from ANOVA for Weighted Average Air Toxic Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

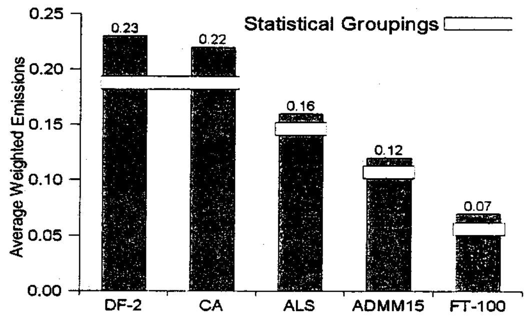

Figure 3. Test Fuel Weighted Average Soluble Organic Fraction Mass Emissions (g/kWh)

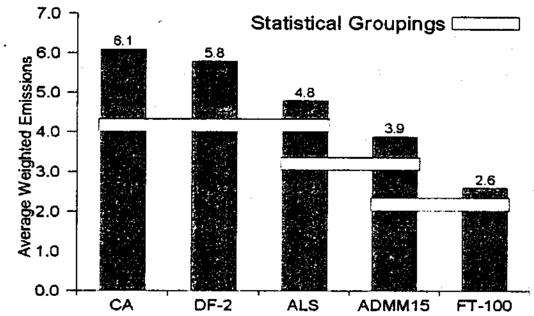

Figure 5. Test Fuel Weighted Average 1,3-Butadiene Emissions (mg/kWh)

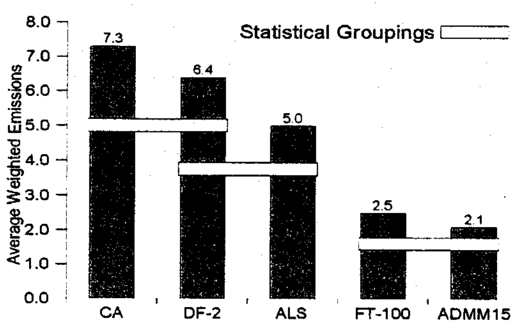

Figure 4. Test Fuel Weighted Average Benzene Emissions (mg/kWh)

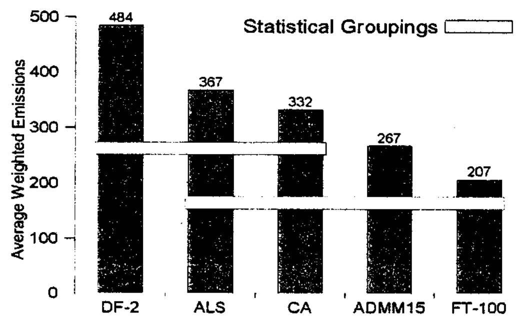

Figure 6. Test Fuel Weighted Average Formaldehyde Emissions (mg/kWh)

Several statistically significant trends, at 95% confidence, were apparent from an ANOVA of the weighted average brake specific emissions data. Table 4 summarizes the qualitative general rank order for the regulated weighted average mass emissions during LPP engine operation with pilot fuel injection turned off. For HC, CO, PM, and SOF the lowest emitting fuels were ADMM15 and FT-100, with the higher emitting fuels being DF-2 then CA. Figure 1 shows the relative levels of test fuel hydrocarbon emissions with statistically similar groupings shown with horizontal bars. The statistical groupings and relative levels of particulate matter emissions are shown in Figure 2 for the test fuels. The relative SOF levels of the particulate matter and their statistical groups are represented in Figure 3. The highest NO_x emitter was DF-2, followed jointly by ADMM15, FT-100, and CA, with ALS being the lowest NO_x emitting fuel.

Table 5 is the qualitative ranking of the test fuels for the four EPA Clean Air Act toxic compounds. Figure 4 shows the ranking and statistically significant similar groupings (horizontal bars) for

Rank	Naphthalene	Acenapthylene	Acenapthene	Fluorine	Phenanthrene
Highest	DF-2	CA	DF-2	DF-2	DF-2
	CA	DF-2	CA	CA	CA
	FT-100	FT-100	FT-100	ADMM15	FT-100
	ADMM15	ADMM15	ADMM15	FT-100	ALS
Lowest	ALS	ALS	ALS	ALS	ADMM15

Rank	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthra-cene	Chrysene
Highest	DF-2	DF-2	DF-2	DF-2	DF-2
	CA	ALS	ALS	CA	CA
	FT-100	CA	CA	ALS	ALS
	ADMM15	FT-100	FT-100	FT-100	FT-100
Lowest	ALS	ADMM15	ADMM15	ADMM15	ADMM15

Rank	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(e)pyrene
Highest	DF-2	DF-2	DF-2
	ALS	CA	CA
	CA	ALS	ALS
	ADMM15	ADMM15	FT-100
Lowest	FT-100	FT-100	ADMM15

Table 6. Fuel Rank Order from ANOVA for Weighted Average Particulate Matter PAH Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

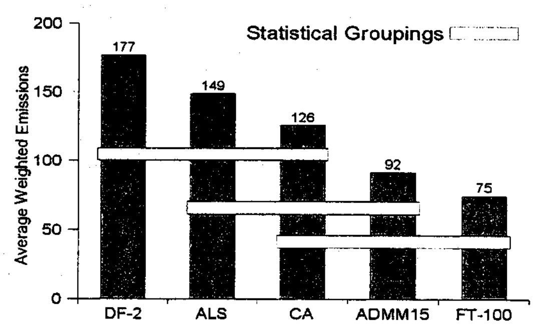

Figure 7. Test Fuel Weighted Average Acetaldehyde Emissions (mg/kWh)

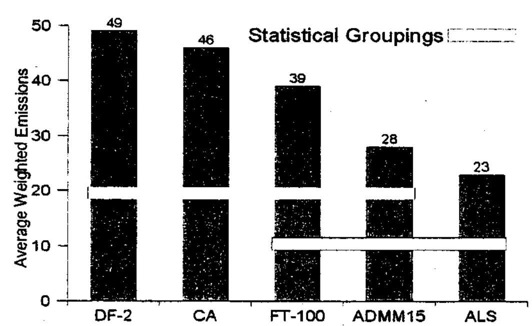

Figure 8. Test Fuel Weighted Average Particulate Phase Naphthalene Emissions (μg/kWh)

benzene emissions. For 1,3-butadiene the lowest emitting fuels were FT-100 and ADMM15, then ALS, with the highest emitting fuels being DF-2 and CA; the statistical groupings are shown in Figure 5. The highest formaldehyde and acetaldehyde emitter was DF-2, followed by ALS, CA, then jointly by ADMM15 and FT-100. Figure 6 shows the relative levels and statistical groupings for formaldehyde. The corresponding groupings for acetaldehyde are shown in Figure 7. For the EPA air toxic compounds, ADMM15 and FT-100 were statistically similar emitting fuels, and always in the lowest grouping for LPP operation with pilot fuel injection turned off.

The fuel rankings for thirteen of the particulate bound soluble phase PAH compounds are shown in Table 6. Due to non-detects, four PAH compounds are being analyzed again with a higher-resolution instrument. The four compounds being reanalyzed

Rank	Naphthalene	2-Methyl-napthalene	1-Methylnaphthalene	2,6-Dimethyl-naphthalene	Acenaphthyl-ene
Highest	CA	DF-2	DF-2	DF-2	DF-2
	DF-2	CA	CA	CA	ALS
	ALS	ALS	ALS	ALS	CA
	ADMM15	ADMM15	ADMM15	ADMM15	ADMM15
Lowest	FT-100	FT-100	FT-100	FT-100	FT-100

Rank	Acenapthene	Fluorene	Phenan-threne	Anthracene	Fluoranthene	Pyrene
Highest	DF-2	DF-2	DF-2	DF-2	DF-2	DF-2
	CA	CA	CA	CA	CA	CA
	ALS	ALS	ALS	ALS	ALS	ALS
	ADMM15	FT-100	FT-100	ADMM15	ADMM15	FT-100
Lowest	FT-100	ADMM15	ADMM15	FT-100	FT-100	ADMM15

Table 7. Fuel Rank Order from ANOVA for Weighted Average Gas Phase PAH Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

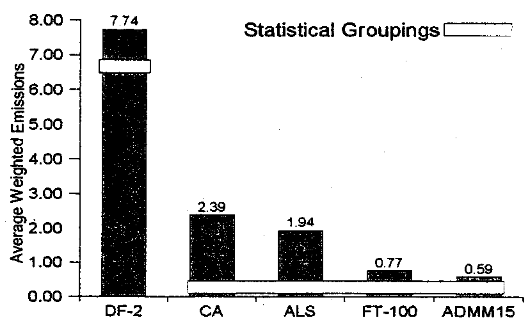

Figure 9. Test Fuel Weighted Average Particulate Phase Chrysene Emissions (μg/kWh)

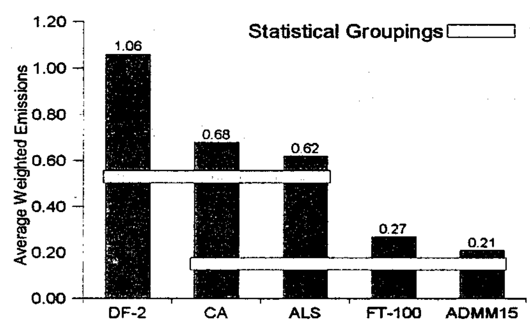

Figure 10. Test Fuel Weighted Average Particulate Phase Benzo(e)pyrene Emissions (μg/kWh)

are benzo(a)pyrene, indeno(123-cd)pyrene, dibenzo(a-h)anthracene, and benzo(ghi)perylene. Figure 8 shows the statistical groupings for the PAH naphthalene bound to the particulate matter. Figure 9 is the statistical groupings for the particulate phase PAH chrysene. The emissions of particulate bound PAH benzo(e)pyrene are shown in Figure 10, along with the statistical groupings. For the majority of PAH compounds, DF-2 fuel was statistically different from the other test fuels. The ADMM15 and FT-100 fuels were in the statistically equivalent (95% confidence) lowest grouping for particulate bound PAH compounds.

The gas phase PAH emissions rank the test fuels qualitatively in the general order shown in Table 7. The gas phase PAH naphthalene mass emissions are shown in Figure 11 along with the statistical groupings. In general, the other gas phase PAH compounds had statistical groupings similar to naphthalene.

Statistical groupings for engine control strategy, which includes pilot fuel injection effects, from an ANOVA for modes 10 and 11 are shown in Figure 12 for particulate matter emissions and in Figure 13 for NO_x emissions. For the least square means of the combined modal and fuel data, each engine control approach was statistically unique for PM and NO_x. The air toxic benzene response in Figure 14 indicates the two pilot conditions are statistically similar, but different from LPP operation with pilot turned off. The LPP with pilot off was statistically the lowest control strategy for the four air toxic emissions. The

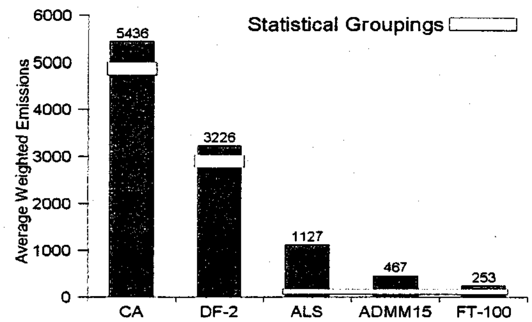

Figure 11. Test Fuel Weighted Average Gaseous Phase Naphthalene Emissions (μg/kWh)

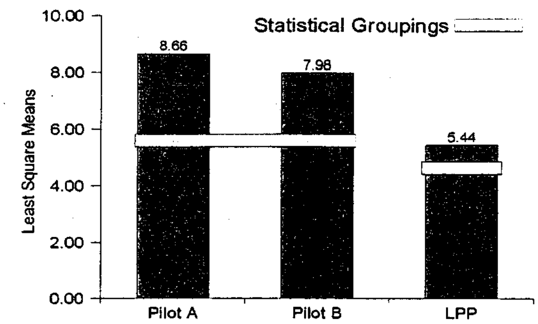

Figure 14. Pilot Fuel Injection Effect on Air Toxic Benzene Emissions (mg/kWh)

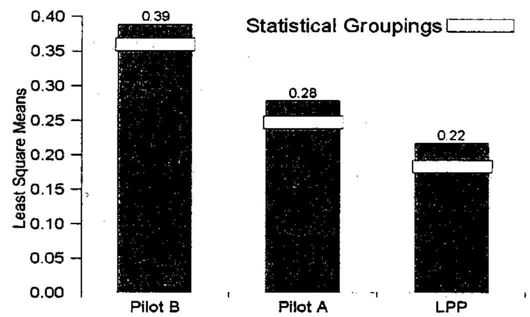

Figure 12. Effect of Pilot Fuel Injection on PM Emissions (g/kWh)

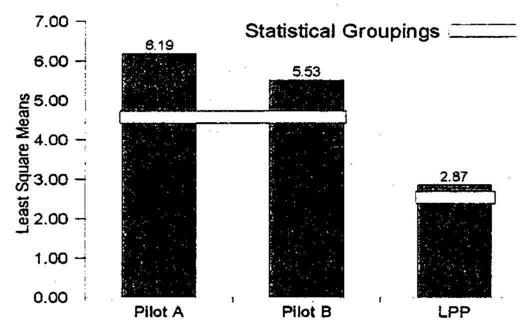

Figure 15. Pilot Fuel Injection Effect on Particulate PAH Chrysene Emissions (μg/kWh)

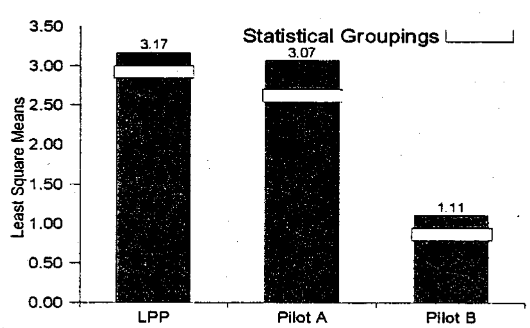

Figure 13. Effect of Pilot Injection on NO_x Emissions (g/kWh)

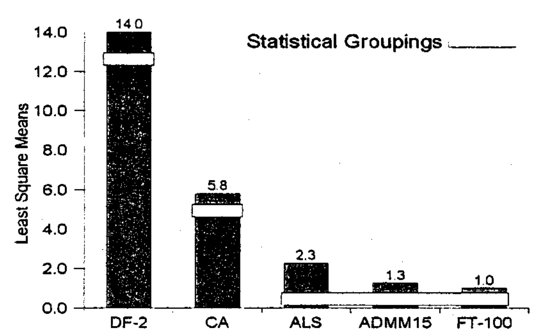

Figure 16. Test Fuel Least Square Means for Pilot Fuel Injection for Particulate PAH Chrysene Emissions (μg/kWh)

particulate bound PAH chrysene emissions in Figure 15 show pilot operation to be different from LPP operation. The same statistical conclusion could be made for the other particulate PAH compounds. The effect of pilot fuel injection on exhaust emissions, compared to the LPP operation with pilot turned off, can be summarized as follows:

- PM emissions increase with pilot fuel injection;
- NO_x emissions decrease with pilot fuel injection;
- Gaseous air toxic levels increase with pilot fuel injection; and

- Both soluble and gas phase PAH increase with pilot fuel injection.

The fuel rank order, along with the statistical groupings for the particulate bound PAH chrysene emissions, is shown in Figure 16. The least square means are calculated by combining the modal and control data. Figure 16 may be compared to Figure 9, which suggests pilot fuel injection increases the PAH chrysene emissions, but the fuel ranking is similar. The other particulate bound and gas phase PAH compounds revealed fuel ranking and relative magnitude results similar to chrysene. The fuel rank order for exhaust emissions with pilot fuel injection operation can be summarized as follows:

- PM rank for ADMM15 and FT-100 lowest, with DF-2 highest;
- NO_x rank is FT-100 lowest, ADMM15 middle, and DF-2 highest;
- Gaseous air toxic rank is FT-100 and ADMM15 lowest, with DF-2 highest; and
- Both soluble and gas phase PAH rank is FT-100 and ADMM15 statistically similar as lowest, with DF-2 the highest emitting fuel.

Conclusions

- ADMM15 or FT-100 had the lowest overall weighted average emission response of the test fuels.
- ADMM15 fuel was statistically the same as FT-100 fuel for toxic, PM, and PAH emissions.
- Pilot fuel injection changes the magnitude of the emission response, but does not significantly alter the fuel rank order.

List of Presentations

1. Yost, D.M. and E.A. Frame, "Particulate Matter Analysis from an Advanced Diesel Engine", CIDI Engine Combustion, Emission Control, and Fuels R & D, Merit Review and Peer Evaluation, Argonne National Laboratory, 22-24 May 2000.

List of Acronyms

ADMM15	15% by Volume DMM blended in ALS Fuel
ALS	Low Sulfur Diesel Fuel
ANOVA	Analysis of Variance
ATDC	After Top Dead Center
BSFC	Brake Specific Fuel Consumption
CA	California Reference Diesel Fuel
DF-2	EPA Certification Diesel Fuel
DMM	dimethoxymethane
DNPH	Dinitrophenylhydrazine
FT-100	Neat Fischer-Tropsch Fuel
IMEP	Indicated Mean Effective Pressure
LPP	Location of Peak Pressure
NO_x	Oxides of Nitrogen
PAH	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter
RPECS	SwRI Rapid Prototyping Electronic Control System
SOF	Soluble Organic Fraction